

# Thursday Morning, November 3, 2011

## Transparent Conductors and Printable Electronics

### Focus Topic

Room: 106 - Session TC+AS+EM-ThM

## Transparent / Printable Electronics Part 1

Moderator: R. Haasch, University of Illinois at Urbana Champaign

8:00am **TC+AS+EM-ThM1 Growth Characteristic and Films Properties of Ga doped ZnO (GZO) by Low Temperature Atomic Layer Deposition, T.W. Nam, JM. Kim, W.S. Lee, H. Kim, Yonsei University, Republic of Korea**

Atomic layer deposition (ALD) has great benefits over other deposition techniques since its growth mechanism controlled by a self-limited surface reaction exhibits excellent conformality, large area uniformity, and atomic scale thickness controllability. In particular, ALD becomes increasingly more promising thin film deposition method for future flexible electronics. Recently, there have been many research efforts on the investigation of doped ZnO for transparent conducting oxides (TCOs) due to their higher mobility than that of undoped ZnO. Ga doped ZnO (GZO) is one of the promising material for substitution of ZnO. As a representative TCO for applications to the transparent thin film transistor (TTFT) or flexible electronic, GZO thin films by PVD or CVD have been extensively studied. Nevertheless studies on GZO films grown by ALD at low temperature condition which can be applied to flexible devices were still not carried out as far as we know in spite of its potential importance. Hence, for this study, we investigated the growth characteristics and film properties of low temperature ALD (LT-ALD) GZO films by varying deposition method. Field emission scanning electron microscopy (FE-SEM) observation of the GZO films deposited on 5:1 via patterns showed that the film has excellent conformality with over 95 % coverage even at room temperature growth. Additionally, the chemical and microstructural analysis was studied by various analytical techniques including X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and atomic force microscope (AFM). Also spectrophotometer was used to measure a transmittance of the film and showed high transmittance that could be applicable to transparent devices.

8:20am **TC+AS+EM-ThM2 Enhancement of C-Axis Orientation of Ga-doped ZnO Films Deposited on Unintentionally Heated Glass Substrates using Nanosheet Seed Layers, H. Makino, Kochi Univ. of Tech., Japan, T. Shibata, NIMS, Japan, N. Yamamoto, Kochi Univ. of Tech., Japan, T. Sasaki, NIMS, Japan, T. Yamamoto, Kochi Univ. of Tech., Japan**

Ga-doped ZnO (GZO) film is one of promising candidates as substitute for ITO transparent electrodes in optoelectronic devices. Control of structural properties, especially c-axis orientation, is crucial issue to improve electrical properties of polycrystalline GZO films on glass or plastic substrates [1]. Recently, nanosheet seed layers were proposed to control crystal orientation of oxide films on amorphous substrates [2]. In this study, we employed a seed layer of tungsten oxide nanosheets with two-dimensional hexagonal lattice structure for deposition of GZO thin films on unintentionally heated glass substrates.

The nanosheets were assembled on glass substrates by Langmuir-Blodgett method. The GZO films with thickness of 100 nm were deposited by an ion-plating with direct current arc discharge on unintentionally heated glass substrates with and without the nanosheet seed layers.

The crystal structural properties were characterized by x-ray diffraction measurements. The c-axis orientation of the GZO films was drastically enhanced by the nanosheet seed layers. The intensity of (002) diffraction peak of GZO films deposited with the seed layers was about 40 times as strong as that deposited without the seed layers. The degree of c-axis orientation was evaluated by the (002) x-ray rocking curve (XRC). The full-width half-maximum of XRC of the GZO films on the nanosheet seed layers was 2.6 °, which is even lower than that of GZO films deposited on bare glass substrate at 200 °C.

The electrical properties were characterized by Hall effect measurements at room temperature. The GZO films deposited on the nanosheet seed layers showed the resistivity of  $2.9 \times 10^{-4} \Omega\text{cm}$  with the Hall mobility of  $24 \text{ cm}^2/\text{Vs}$  and the carrier concentration of  $9.0 \times 10^{20} \text{ cm}^{-3}$ . On the other hand, the GZO film deposited without the nanosheet seed layers showed the resistivity of  $5.0 \times 10^{-4} \Omega\text{cm}$  with the Hall mobility of  $17 \text{ cm}^2/\text{Vs}$  and the carrier concentration of  $7.2 \times 10^{20} \text{ cm}^{-3}$ . Both the Hall mobility and the carrier concentration were improved by the nanosheet seed layers.

[1] T. Yamada et al., J. Appl. Phys. 107, 123534 (2010). [2] T. Shibata et al., Adv. Mater. 20, 231 (2008).

8:40am **TC+AS+EM-ThM3 Multi-component Transparent Conducting Oxides: Progress in Materials Modeling, S.-H. Wei, National Renewable Energy Laboratory**

Transparent conducting oxides (TCOs) play an essential role in modern optoelectronic devices through their combination of electrical conductivity and optical transparency. We review recent progress in our understanding of multi-component TCOs formed from solid solutions of ZnO, In<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>, with a particular emphasis on the contributions of materials modeling, primarily based on Density Functional Theory. In particular, we highlight three major results from our work: (i) the fundamental principles governing the crystal structures of multi-component oxide structures including (In<sub>2</sub>O<sub>3</sub>)(ZnO)<sub>n</sub>, named IZO, and (In<sub>2</sub>O<sub>3</sub>)<sub>m</sub>(Ga<sub>2</sub>O<sub>3</sub>)<sub>l</sub>(ZnO)<sub>n</sub>, named IGZO; (ii) the relationship between elemental composition and optical and electrical behavior; (iii) the origin of high-performance of amorphous oxide semiconductors. From these advances, the challenge of the rational design of novel electroceramic materials is discussed.

9:20am **TC+AS+EM-ThM5 Composition Control of Electron Beam Deposited Nb-TiO<sub>2</sub> Thin Films, N.A. Beckers, R.T. Tucker, University of Alberta, Canada, M.D. Fleischauer, NRC-National Institute for Nanotechnology, Canada, M.J. Brett, University of Alberta, Canada**

Nb-doped TiO<sub>2</sub> has been identified as a potential indium-free transparent conductor, and has been fabricated by pulsed laser deposition and sputtering with good success.<sup>1,2</sup> Other deposition methods, such as electron beam evaporation, are of interest for this material but have had limited demonstration to date. It would be advantageous to be able to use electron beam evaporation because in addition to planar films, the collimated flux allows for structured thin films via glancing angle deposition (GLAD). Composition control is essential for doped functional materials, which is typically difficult to obtain through physical mixing of source materials. Here we show that using a sol gel approach to prepare the source materials provides a possible route to circumvent this issue. The facile, solution based sol gel process for the synthesis of ceramic and glassy materials allows for precise composition control by controlling the amounts and ratios of the metal oxide precursors. A sol gel methodology was used to prepare a series of Nb-doped TiO<sub>2</sub> deposition source materials with the following compositions: Nb<sub>0.06</sub>Ti<sub>0.94</sub>O<sub>2</sub>, Nb<sub>0.12</sub>Ti<sub>0.88</sub>O<sub>2</sub>, and Nb<sub>0.24</sub>Ti<sub>0.76</sub>O<sub>2</sub>. We will show that XPS results confirm the composition of the electron beam deposited films and reflects the composition of the source materials. Premixed powders of Nb<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> do not show the same translation of composition as the sol-gel derived source material. Details on the effects of the post-deposition annealing environment on the thin film optical and electrical properties will also be presented.

### References:

1. Yamada, N.; Hitosugi, T.; Hoang, N. L. H.; Furubayashi, Y.; Hirose, Y.; Konuma, S.; Shimada, T.; Hasegawa, T. *Thin Solid Films* **2008**, *516*, 5754-5757.

2. Ishida, T.; Okada, M.; Tsuchiya, T.; Murakami, T.; Nakano, M. *Thin Solid Films* **2011**, *519*, 1934-1942.

9:40am **TC+AS+EM-ThM6 Laboratory and Production-Scale Low-Temperature Transparent Conducting Oxide Deposition, E. Ritz, University of Illinois at Urbana Champaign, G.B. Rayner, Kurt J. Lesker Company, D. Andruczyk, University of Illinois at Urbana Champaign, T. Dockstader, Kurt J. Lesker Company, D.N. Ruzic, University of Illinois at Urbana Champaign**

Transparent conducting oxides (TCOs) are a class of materials that are becoming increasingly ingrained in our daily lives due to their use in electronic displays and mobile devices. There is a strong need to develop an economical deposition technique that allows for high transparency films with high electrical conductivity while replacing costly materials such as Indium Tin Oxide (ITO) with alternatives such as Aluminum-doped Zinc Oxide (AZO). In addition, a low-temperature deposition method would allow creation of TCOs on flexible plastic substrates, such as polyethylene terephthalate (PET). By using a dual DC magnetron system with a secondary RF antenna running at 13.56 MHz, a process has been developed that can deposit TCO films without significantly heating the substrate while maintaining high transmission and electrical properties. This capability has been demonstrated on a small-scale experimental setup utilizing 3-inch diameter circular magnetrons as well as a prototype production-scale chamber operating with 18x3.5 inch rectangular magnetrons aimed at flexible photovoltaic manufacturing. Using an immersed inductive RF antenna, ionization fraction can be increased to over 80%, measured by a

gridded energy analyzer, and plasma density increased by an order of magnitude from  $10^{10}$  cm<sup>-3</sup> to  $10^{11}$  cm<sup>-3</sup>, as measured by Langmuir probe. The secondary plasma deposits energy in the film without heating the substrate above 100°C while still achieving film resistivity on the order of  $10^{-3}$ - $10^{-4}$  Ohm-cm (measured by four-point probe method) and transparency of greater than 90% in the visible wavelengths (measured by spectrophotometry.) Adjusting the RF power (0-1000W) and the oxygen content (0-5%) in the plasma enables the ability to tune the film transparency and conductivity to desired levels. Crystal formation of films analyzed by x-ray diffraction (XRD) and elemental composition determined by x-ray photoelectron spectroscopy (XPS).

10:40am **TC+AS+EM-ThM9 Optical and Electronic Properties of Photonic Crystal Based Transparent Conductors**, *S. Narayanan, M. Bockstaller, L. Porter*, Carnegie Mellon University

Transparent conductors are becoming ubiquitous in a host of civil and military applications, including transparent electrical contacts in solar cells and LEDs, heated glass for aircraft and automobile windows, and electrochromic devices and smart windows. However, finding abundant materials with optimal electrical and optical properties and that can be produced economically is a particular challenge. Moreover, limited supply and large demand, of late, for indium has inspired focused research on finding alternatives to ITO as a transparent conductor. We report here a novel approach to control optical properties such as absorption, transmission and reflection in multilayered structures (based on [1-2]) with absorbing components. Appropriate combination of materials could, among others, allow for applications like transparent electrodes, transparent electromagnetic shielding, flexible transparent conductors, etc. Through this study, we have demonstrated the validity of this approach using a few different materials combinations including polymer/metal and metal/ceramic systems. In these realizations the approach was shown to increase the transparency in the visible frequency range by ~ 3 orders of magnitude as compared to the reference materials. For example, transmittances of 30-50% of incident light in the visible region were measured for films containing a polymer (polystyrene – PS) and an amount of metal (gold – Au) that was 3-4 times as thick as its skin depth (~ 40-50 nm). We have also found compatibility between the observed experimental results and numerical simulations. Apart from enhanced optical transmittance, resistivity values of ~  $10^{-4}$  Ωcm (comparable to Au films having ~  $10^{-5}$  Ωcm) have also been discovered in structures having insulating components. Our ongoing and future work is focused on alternative structures to enhance conductivity in the transverse direction as well as incorporate flexibility in the same. **References:** [1] M. Scalora *et al.*, *J. Appl. Phys.* **83** 5 (1998) 2377-2383 [2] M. Scalora, M. J. Bloemer, C. M. Bowden, *Optics and Photonics News* **10** 9 (1999) 24-27

11:00am **TC+AS+EM-ThM10 Effect of Plasma Treatment and Annealing on the Electrical Properties of Spin-Coated Colloidal ITO Films**, *S.M. Joshi, G.W. Book, R.A. Gerhardt*, Georgia Institute of Technology

Colloidal ITO based inks may be an attractive route to direct writing transparent circuits and also be useful for the fabrication of transparent conductive ITO films on complex shaped substrates. The presence of stabilizing ligands and minimal contact between the ITO nanoparticles in the deposited films can be a challenge in obtaining the optimum electrical properties. This study investigates the effect of plasma treatment and annealing on the electrical properties of colloidal ITO films. Crystalline colloidal ITO nanoparticles were synthesized in-house by a non-aqueous technique. The solutions were spin coated onto glass and quartz substrates and their electrical and optical properties were evaluated. All films were found to be completely transparent, while the as-deposited films had resistivities more than  $10^8$  ohm-cm. Plasma treatments were shown to be effective in removing residual organics in the films, and even without annealing, some recipes were able to reduce the film resistivity by more than four orders of magnitude. Plasma treatments, when done in combination with annealing, resulted in films with resistivities less than 1 ohm-cm.

11:20am **TC+AS+EM-ThM11 Hybrid Organic/Inorganic Materials and Devices for Flexible Electronics Applications**, *M.A. Quevedo-Lopez, J.I. Mejia, A. Salas-Villasenor, A. Carrillo-Castillo, B.E. Gnade*, University of Texas at Dallas, *D. Allee*, Arizona State University **INVITED**

The field of flexible electronics has expanded tremendously over the past few years. Similar to what happened in silicon integrated circuit technology 40 years ago; flexible electronics are now at a point where system design and process integration will drive the technology. Flexible electronics will likely push the limits of material performance, process integration, circuit design, and system integration to demonstrate the full potential of flexible electronics. In general, key components for any flexible electronic application include thin film transistors. In order to be competitive with

state-of-the-art a:Si:H thin film transistors, any other thin film transistor technology must show reproducible transistor parameters such as mobility, threshold voltage, drive current and reliability.

A grand challenge in flexible, thin-film-transistor (TFT) circuitry is the development of complementary metal oxide semiconductor (CMOS) circuits. Although flexible digital circuits, flexible sensors, flexible batteries and solar cells have already been demonstrated, the missing technology piece that must be developed is flexible analog circuitry. For example, an operational amplifier will enable the interface to most sensors and actuators, significantly expanding the functionality of flexible electronic systems. In this paper, we will present n- and p-type chalcogenide-based materials that can be used as the building blocks for analog CMOS-based circuits. In particular, we will introduce the use of chemical bath deposition as an alternative to deposit these materials and will discuss the correlation between device characteristics and materials properties. Photolithography-based chalcogenide-based TFTs processed by chemical bath deposition achieved mobilities in the order of 10-25 cm<sup>2</sup>/V-s. In addition, we demonstrate hybrid CMOS for a:Si-Pentacene, CdS-Pentacene and CdS-TIPS Pentacene.

We also present the impact of semiconductor thickness, gate dielectrics and contact in device performance. In addition, NAND, NOR and Inverters are demonstrated using chalcogenide-based materials integrated with either a-Si or pentacene. Device processing is carried out at a maximum processing temperature of 110°C, which is compatible with most plastic substrates.

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